V.N.10 Sol-Gel Based Polybenzimidazole Membranes for Hydrogen Pumping Devices

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Objectives

We are studying the concept, behavior and applicability of PBI membranes in electrochemical hydrogen pumps. Membranes are being prepared and analyzed by a variety of techniques (microscopy, NMR, cell performance) to provide data and insights for the development of a model to understand and predict the properties of gel membranes. The concept of a robust and efficient hydrogen pumping device is being tested by incorporating membrane-electrode concepts into working devices and characterizing the device performance in a laboratory environment. Fundamental studies of the transport processes within the membrane are also being conducted by advanced NMR techniques to understand the conduction mechanism and determine the effects of structure, process, and electrolyte composition on the transport phenomena.

Technical Barriers

Electrochemical hydrogen pumping devices have been built and characterized under a variety of conditions. While we have validated the general concept of hydrogen pumping in our proposal, a critical question of the device operation is the level of hydrogen purity that can be obtained from various gas streams. Standard sampling, transport and testing techniques have introduced impurity levels into the exhaust gases that interfere with the purity determinations. On-line gas analysis equipment is needed to accurately test for hydrogen purity from potential feed streams of interest from the perspective of the future hydrogen economy.

Abstract, Progress Report and Future Directions

Electrochemical Hydrogen Pumping

The basic concept of electrochemical pumping using a high temperature membrane has been demonstrated. Low concentrations of hydrogen can be purified, as shown by operation on a stream containing 35% hydrogen. The benefits of high temperature operation have been shown by purifying hydrogen in the presence of high amounts of contaminants, most notably CO in a synthetic natural gas reformate. Humidified and non-humidified feed streams have been administered to the pump and polarization curves have been generated providing the first electrochemical characterization of the device. While being humidified, there is an increase in pump performance. It is proposed that this is related to a decrease in electrode resistance. These initial tests exhibit excellent durability of greater than 1,000 hrs in multiple cells operated under different conditions. Faradic flows have been observed at higher current densities.

Preliminary gas chromatography has been performed on the outlet streams and indicates increases in hydrogen and substantial decreases in carbon monoxide and carbon dioxide concentrations. At this time, specific purity and concentration values are difficult to obtain without on-line gas chromatographic instrumentation. Some early modeling efforts have been initiated on the effects of structure and mobility on transport.

Polymer film preparation and morphology

The morphology of the polybenzimidazole (PBI) films is believed to aid in its high proton conductivity and is an important part of this project. We have established a promising partnership with Oak Ridge National Laboratory (Karren More) and have sent a student to Oak Ridge for a one-month training program. This student will spend nearly the entire summer of 2007 as a visiting worker at ORNL in Dr. More's laboratory. The sample preparation of the PBI films is very sensitive to the material used as a substrate for film casting. Reaction products were actually observed between the phosphoric acid and glass plates. Also, mechanical

forces used to hold the membrane flat are believed to introduce artifacts into the images. The morphology of the PBI films will continue to be investigated in the summer of 2007.

Two sets of carefully prepared samples were synthesized for NMR measurements. One set of m-PBI samples were prepared to be identical in polymer composition, molecular weight, and phosphoric acid concentration. The only difference in this set of samples was the method of preparation, i.e., PPA process versus conventional imbibing. The NMR analysis of these samples is described below. The next set of samples that were designed to look at the effects of polymer structure (all prepared by the PPA process) have been prepared and are currently under investigation by NMR techniques.

NMR measurements

Mass transport phenomena in phosphoric acid, an important fuel cell compound, of varying concentration were studied by multinuclear NMR measurements including pulsed gradient spin-echo (PGSE) and static field gradient techniques. The latter method was developed in order to be able to measure self-diffusion as a function of applied hydrostatic pressure. The high pressure measurements were carried out at 288 K, and variable pressure up to 2.5 kbar. The high pressure data were obtained for four different concentrations of phosphoric acid in water in the range of 6% - 100% by weight. The calculated activation volume for ^{1}H nuclei, increasingly dominated by the water protons, decreased as the acid concentrations decreased, exhibiting behavior approaching that of liquid bulk water. In addition ^{31}P data show higher activation volumes than the corresponding ^{1}H data, mainly due to the larger molecular size of the phosphate groups compared to water molecules. This difference is a factor of two for 100% acid, suggesting a proton transport mechanism for high concentration acid which involves the hopping transfer of protons between the larger phosphate groups. Using ^{1}H and ^{31}P pulsed gradient spin-echo techniques, self-diffusion coefficients have been measured for a range of phosphoric acid concentrations (6~100 wt %) over the temperature region from 293 to 363 K. The data show again that protons diffuse faster than the phosphorus carrying species. Different activation energies were obtained above and below 12 wt % acid concentration, suggesting the presence of ion association effects at this concentration.

Additional studies were then conducted to look at proton and phosphorus mobilities in PBI-PA membranes. Mass transport studies of proton-conducting phosphoric acid (PA) doped *meta*-polybenzimidazole (PBI) fuel cell membranes were examined. In this study, the fundamental differences in transport properties between *m*-PBI/PA membranes prepared by conventional imbibing procedures and the polyphosphoric acid (PPA) process were explored. These comparative studies were designed to isolate the method of membrane preparation (PPA process versus conventional imbibing) as the sole variable in the study. The membranes were characterized by proton conductivity and multinuclear (^{1}H and ^{31}P) nuclear magnetic resonance (NMR) measurements. Both short-range and long-range dynamical processes were investigated by spin-lattice and spin-spin relaxation time measurements, and by pulsed field gradient diffusion, respectively. Comparative data for pure PA and polyphosphoric acid were included in the analysis. The high proton conductivity (0.13 S/cm at 160°C) of the PPA processed membranes is correlated with rapid proton self-diffusion ($3x10^{-6}$ cm^2/s at 180°C). The ^{31}P results reveal the presence of both PA and the dimeric pyrophosphoric acid and indicate strong interaction between the phosphate groups and the *m*-PBI matrix, with negligible anionic transport for both kinds of membranes. The higher concentration of PA in the PPA membrane provides an additional proton transport mechanism involving rapid exchange between the PA and pyrophosphoric acid species.

Publications

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3. *Determination of the Molecular Parameters and Studies of the Chain Conformation of Polybenzimidazole in DMAc/LiCl*, C.B. Shogbon, J.-L. Brousseau, H. Zhang, B.C. Benicewicz, Y.A. Akpalu, *Macromolecules*, **2006**, *39*, 9409-9418.

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5. *Computer Simulations of Ionomer Structure and Dynamics*, M. Goswami, S.K. Kumar, A. Battacharya, submitted.